ELSEVIER

Atmospheric Research 57 (2001) 43–49

ATMOSPHERIC RESEARCH

www.elsevier.com/locate/atmos

Observation of ozone concentration during the solar eclipse

S. Chudzyński [a], A. Czyżewski [a], K. Ernst [a], A. Pietruczuk [a], W. Skubiszak [a], T. Stacewicz [a,*], K. Stelmaszczyk [a], A. Szymański [a], I. Sówka [b], A. Zwoździak [b], J. Zwoździak [b]

[a] *Institute of Experimental Physics, Warsaw University, 00-681 Warsaw, Hoża 69, Poland*
[b] *Faculty of Environmental Engineering, Technical University of Wrocław, Wybrzeże Street, Wyspiańskiego 27, 50-370 Wrocław, Poland*

Received 3 March 2000; accepted 8 October 2000

Abstract

We report the results of measurements of ozone concentrations during the solar eclipse of 11 August 1999. The experiment was performed in Warsaw (Poland) and its surroundings. The temporal evolution of ozone concentration was measured using the differential absorption lidar (DIAL) and it was compared with results obtained by several monitoring stations measuring with other methods. In almost all cases, a drop in the ozone concentration was observed during the eclipse. Experimental data was compared with calculations done using a simple model based on NO_x–O_3 chemical kinetics.

Keywords: Ozone monitoring; Eclipse; Chemical kinetics

1. Introduction

Researchers are still largely interested in the problem of tropospheric ozone. Its background concentration reaches a mean value of about 20 ppb (Crutzen, 1995) and is mainly of stratospheric origin. The remaining part of ozone is produced as a result of chemical reactions occurring in the troposphere. In urban areas, substrates for these reactions (NO_x and other compounds) are of anthropogenic origin, mainly as a result of

* Corresponding author. Fax: +48-22-6256404.
E-mail address: tadstac@fuw.edu.pl (T. Stacewicz).

PII: S0169-8095(00)00071-5

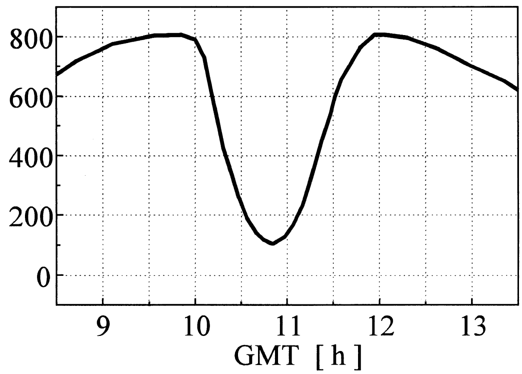

Fig. 1. Evolution of sun light intensity [W/m^2] during the solar eclipse that was assumed for calculations of O_3–NO_x dynamics.

the combustion of various fuels. The most efficient reactions involving the ozone are driven by solar radiation (Finlayson-Pitts and Pitts, 1986; Seinfeld and Pandis, 1998).

The solar eclipse provided a unique possibility to check our comprehension of the ozone creation/degradation mechanisms. During the eclipse, the character of changes in sun light intensity strongly differs from those occurring between night and day. Diurnal variations of radiation are relatively slow and are accompanied by other phenomena, like time-dependent changes of the sunlight spectrum. During the eclipse, the solar disc is geometrically hidden by the moon, so that the light is "switched" off and on relatively quickly, without additional spectral effects. Investigations of the ozone photochemistry could be then performed on a "short time" scale.

Table 1
Description of monitoring stations

No.	Figure	Location—street	Description of location	Altitude	Technique
1	2a	Belsk	Village, 50 km south of Warsaw	Ground station	Chemiluminescence
2	2b	Jarczew	Village, 80 km southeast of Warsaw	Ground station	Chemiluminescence
3	2c	Warsaw—Podleśna	Suburb area	Ground station	Chemiluminescence
4	2d and 3	Warsaw—Jerozolimskie	The city center, the most intense traffic area in Warsaw	15 m above the street level, 330 m optical path length	DOAS
5	2e	Warsaw—Pasteura	The town, traffic	300 m above street level	DIAL

The laboratories belong to the following institutions: (1) Geophysical Observatory of Polish Academy of Science, (2) and (3) Institute of Meteorology and Water Resources, (4) Voivodship Inspectorate for Environmental Protection in Warsaw, (5) Optics Division of Institute of Experimental Physics, Warsaw University.

In Poland, the solar eclipse of 11 August 1999 was only partial. In Warsaw, it started at 9:56 am and it was over at 11:56 am GMT. The maximum cover of the sun disc was observed at 10:50 am and it reached 87%. In Fig. 1, the evolution of the sunlight intensity during the eclipse is presented. The curve is based on geometrical considerations. The normalization of the data to the circumstances corresponding to the region of Warsaw was done due to measurements of the radiation intensity performed in monitoring station in Jarczew (see Table 1).

2. Experiment

Observations of the ozone concentrations were done in Warsaw and its surroundings. A description of the detectors, their localization and method of measurements is presented in Table 1.

Chemiluminescence technique is used for monitoring O_3 and NO_x in point detectors (Alloway and Ayres, 1998). In the differential optical absorption spectroscopy (DOAS) method, the selective detection of gas species is done by the analysis of absorption

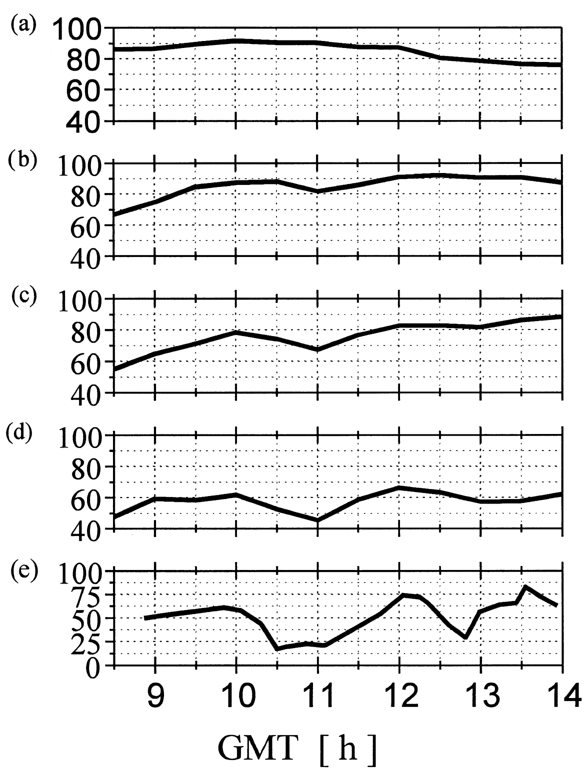

Fig. 2. Ozone concentration measured during the solar eclipse by the following laboratories: (a) Belsk, (b) Jarczew, (c) Warsaw—Podleśna, (d) Warsaw—Jerozolimskie, (e) Warsaw—Pasteura. All values are given in [$\mu g/m^3$].

within a wide spectral range on a long absorption path (Siegrist, 1994). Description of the differential absorption lidar (DIAL) technique can be found elsewhere (Chudzyński et al., 1997; Killinger and Mooradian, 1983). It is based on the analysis of the lidar echo measured at two wavelengths: one that is tuned to the absorption line of the investigated compound (for O_3 it is equal to 286.3 nm) and the other one (slightly shifted), that is less absorbed and serves as a reference (282.4 nm).

On the day of the eclipse, the DIAL measurements started at 09:00 am and were continued until 2:00 pm GMT. The laser beam was directed above the region of the town of large traffic intensity. The data shown in Fig. 2e corresponds to the effective altitude of about 300 m above street level. The data was averaged over 30 min, similarly to the other detectors.

The meteorological conditions during the measurements were as follows: temperature 27°C, relative humidity about 50%, clear sky condition until 8:00 am and 40% sky coverage between 10:00 am and 6:00 pm.

3. Results of measurements

Results of ozone measurements are presented in Fig. 2a–e. In all cases but one, a decrease of the ozone concentration synchronized with the eclipse time was observed. The highest decrease was measured by DIAL located in Warsaw (Fig. 2e). A smaller dip was registered by the laboratory in Jarczew (Fig. 2b) that is out of town. Other two laboratories located in Warsaw (Podlesna—Fig. 2c, Jerozolimskie—Fig. 2d), also observed a decrease of the ozone concentration. This effect was not registered in the laboratory in Belsk (Fig. 2a), which is situated in a village, with a small influence of traffic and industry.

4. Model

In order to describe the dynamics of ozone changes under the influence of variable sunlight intensity, a simple chemical kinetics model was considered. The model consists of main reactions leading to ozone production and destruction. It is based on the NO_x–O_3 chemistry (Finlayson-Pitts and Pitts, 1986; Seinfeld and Pandis, 1998). The reactions considered and their efficiencies are shown in Table 2.

Table 2
Basic reactions of the ozone production and destruction in the atmosphere (Seinfeld and Pandis, 1998)

	Reaction		Rate coefficients
1	Photo-dissociation of NO_2	$NO_2 + h\nu \rightarrow NO + O$	$j_1 = j_{10} I_n(t)$, $j_{10} = 8.9 \times 10^{-3}$ s^{-1}, $I_n(t)$—sunlight intensity
2	Creation of ozone in the presence of a third body (M)	$O + O_2 + M \rightarrow O_3 + M$	$k_2 = 6 \times 10^{-34}$ (cm^6)/(mol$^2 \cdot$ s)
3	Destruction of ozone under collision with NO molecule	$O_3 + NO \rightarrow NO_2 + O_2$	$k_3 = 1.8 \times 10^{-14}$ (cm^6)/(mol$^2 \cdot$ s)

On the basis of indicated reactions the rate equations for ozone $[O_3]$, nitrogen oxide [NO], nitrogen dioxide $[NO_2]$ and atomic oxygen [O] concentrations can be written as follows:

$$\frac{d[O_3]}{dt} = k_2[O][O_2][M] - k_3[O_3][NO], \tag{1}$$

$$\frac{d[NO]}{dt} = j_1[NO_2] - k_3[O_3][NO], \tag{2}$$

$$\frac{d[NO_2]}{dt} = -j_1[NO_2] + k_3[O_3][NO], \tag{3}$$

$$\frac{d[O]}{dt} = j_1[NO_2] - k_2[O][O_2][M]. \tag{4}$$

The rate constants of the reactions are given in Table 2.

Adding Eqs. (2) and (3), we get:

$$\frac{d[NO]}{dt} + \frac{d[NO_2]}{dt} = 0 \tag{5}$$

and as a consequence, the following relation:

$$[NO] + [NO_2] = \text{const} = [NO]_0 + [NO_2]_0, \tag{6}$$

where $[NO]_0$ and $[NO_2]_0$ denote the initial values of the relevant species. Eq. (6) makes possible the calculation of [NO] from known $[NO_2]$ values.

In Eq. (1), the unknown term $k_2[O][O_2][M]$ can be found using the relation (4). It is well known that due to the fast destruction of atomic oxygen in the troposphere, in comparison with other substrates, we may assume a steady state approximation:[1]

$$\frac{d[O]}{dt} \to 0. \tag{7}$$

Then, Eq. (4) provides the relation:

$$k_2[O][O_2][M] = j_1[NO_2]. \tag{8}$$

Finally, after using Eqs. (6) and (8), the rate equation for the ozone concentration (Eq. (1)) can be written in the form:

$$\frac{d[O_3]}{dt} = j_{10} I_n(t)[NO_2] - k_3[O_3]([NO]_0 + [NO_2]_0 - [NO_2]). \tag{9}$$

By solving this equation, the temporal evolution of ozone concentration can be found. As nitric dioxide concentrations ($[NO_2]_0$ and $[NO_2]$) we used the empirical data. They mirrored the influence of urban conditions on the investigated process. The $[NO]_0$ was found as a free parameter from the best fit of the equation solution to the experimental data.

[1] The experimentally proven phenomenon of low concentration of atomic oxygen, as well as of the small dynamic of this component, is widely discussed by Seinfeld and Pandis (1998) and by Atkins (1984).

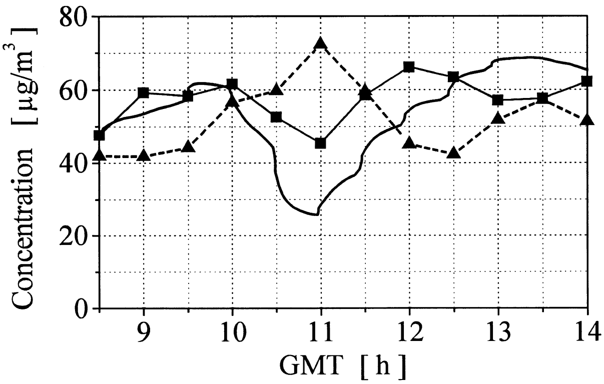

Fig. 3. Comparison of the model results (continuous line) with the ozone concentration (continuous line with squares) measured by the Laboratory of Voivodship Inspectorate for Environmental Protection in Warsaw. Dashed line with triangles shows the NO_2 concentration measured by this station.

We compared the calculations with the experimental results. A quantitative comparison could be done only with data concentrations from the laboratory of Voivodship Inspectorate for Environmental Protection in Warsaw because only this station beside of ozone provided the empirical values of $[NO_2]$ as well. Since the solar radiation intensity was not measured by this laboratory, we assumed for our calculations that $I(t)$ function can be based on purely geometrical considerations related to the eclipse (see Fig. 1).

Results are presented in Fig. 3. Since the experimental data were averaged over 30 min, we applied the same averaging constant to the equation solution. The ozone concentrations are shown together with measured $[NO_2]$ values. The best agreement between the experimental and the model results was found for the $[NO]_0$ of 11 $\mu g/m^3$. Note that changes of $[NO_2]$ values are opposite to changes of the $[O_3]$.

5. Conclusions

In this work, the ozone concentration data from measurements performed in Warsaw (Poland) at the time of the partial sun eclipse (11 August 1999) are presented. The measurements were performed by means of DIAL and DOAS systems as well as by conventional point detectors. The decrease of ozone concentration during the eclipse time was clearly observed. The simple model, based on NO_x–O_3 chemistry, indicates that light intensity is the main factor influencing ozone concentration.

Acknowledgements

This work was partially supported by the Polish Committee for Scientific Research (project Nos. 6 P04G 027 17 and 6 P04G 030 17). We would like to thank the following institutions and persons for providing the data: Mrs. E. Pacholska (Voivodship Inspectorate for Environmental Protection in Warsaw), Mrs. J. Iwanek (Environmental Protection Agency), Mgr. J. Jarosławski (Institute of Geophysics of Polish Academy of Sciences at Belsk) as well as Dr. S. Puchalski and Mgr. P. Sobolewski (Institute of Meteorology and Water Resources).

References

Alloway, B.J., Ayres, D.C., 1998. Chemical Principles of Environmental Pollution. Stanlet Thorns (Publishers), UK.

Atkins, P.W., 1984. Physical Chemistry. Oxford Univ. Press, London.

Chudzyński, S., Ernst, S., Stacewicz, K., Szymanski, T., 1997. Mobile Lidar Laboratory. Proceedings of SPIE, vol. 3188, pp. 180–185.

Crutzen, P.J., 1995. Overview of tropospheric chemistry: developments during the past quarter century and a look ahead. Faraday Discuss. 100, 1–21.

Finlayson-Pitts, B.J., Pitts Jr., J.N., 1986. Atmospheric Chemistry: Fundamentals and Experimental Techniques. Wiley, New York.

Killinger, D.K., Mooradian, A., 1983. Optical and Laser Remote Sensing. Springer-Verlag, Berlin.

Seinfeld, J.H., Pandis, S.N., 1998. Atmospheric Chemistry and Physics. Wiley, New York.

Siegrist, M.W., 1994. Air Monitoring by Spectroscopic Technique. New York–Chichester–Brisbane–Toronto–Singapore.